Molecular Self-Assembly in Alcohol-Water Solutions

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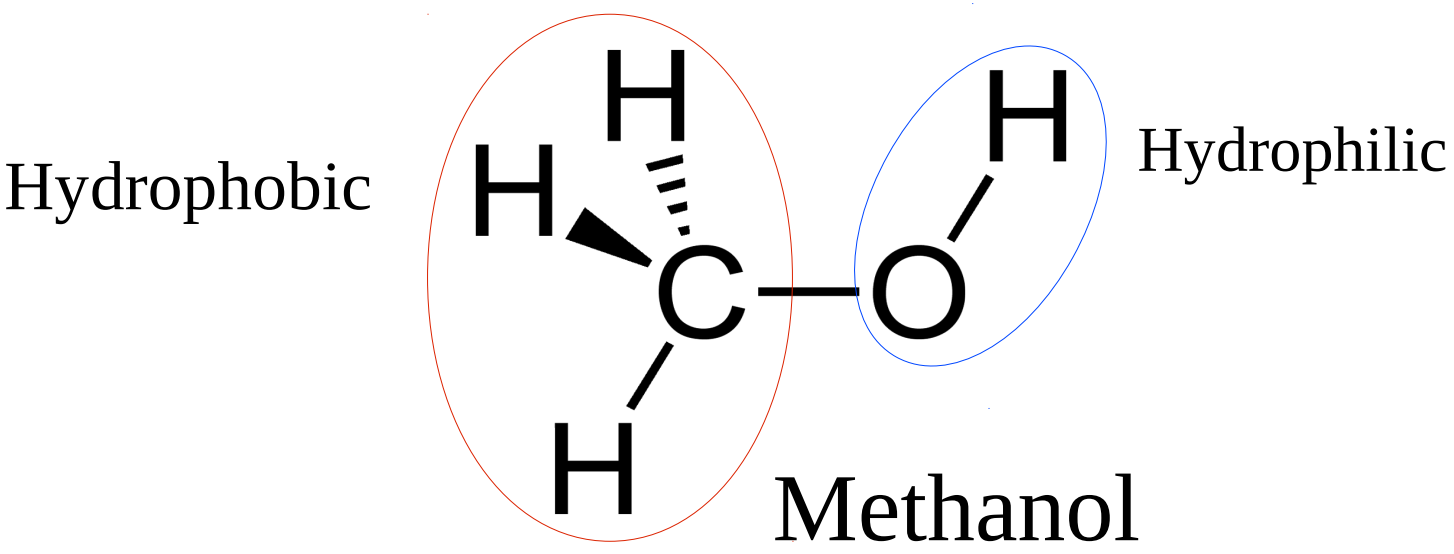
NSF CHRNS Center for High Resolution Neutron Scattering NIST

The Problem

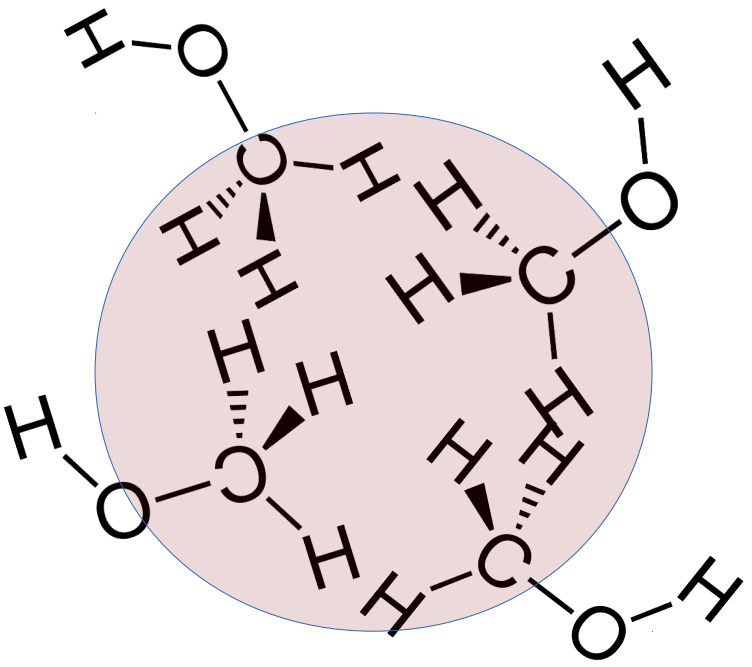
- Simplest amphiphile
- Low entropy in water - methanol (CH_3OH) solutions[1]



[1] H.S. Frank, M.W. Evans, J. Chem. Phys. 13 (1945) 507

Goals

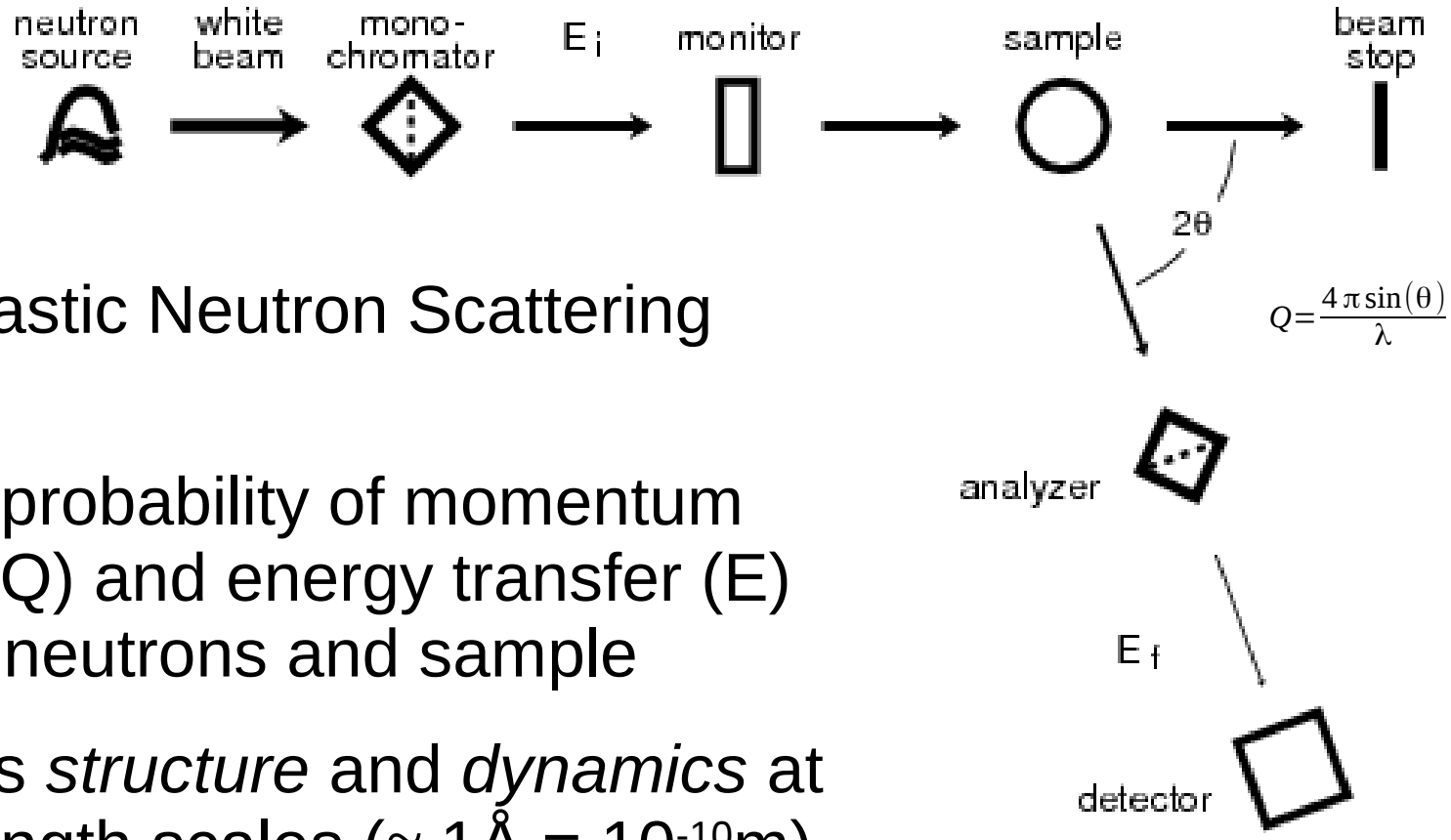
- Confirm existence of clusters[1]
- Investigate temperature dependence of formation
- Investigate cluster dynamics (diffusion, rotation, lifetime)



Possible Methanol Cluster

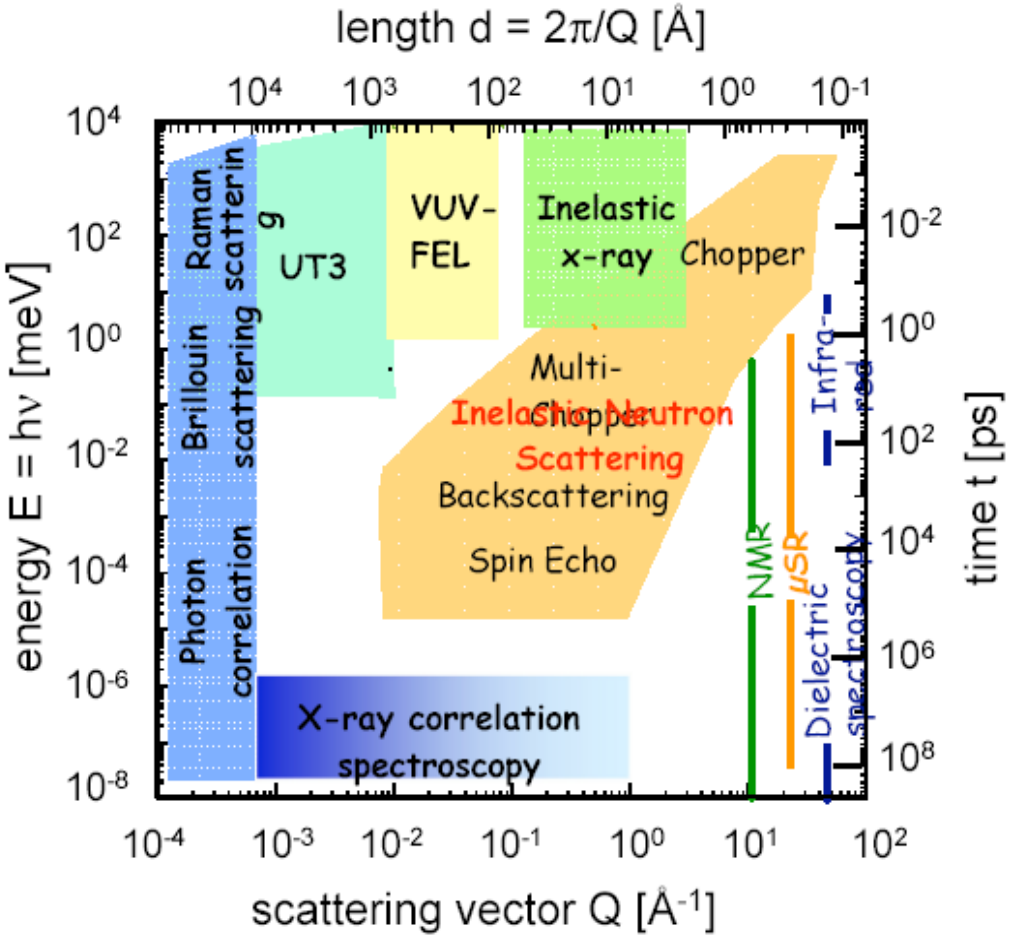
[1]L. Dougan, J. Crain, J.L. Finney, A.K. Soper, Phys. Chem. Chem. Phys. 12 (2010), 10221

Methods – Neutron Scattering



- Quasi-Elastic Neutron Scattering (QENS)
- Records probability of momentum transfer (Q) and energy transfer (E) between neutrons and sample
- Measures *structure* and *dynamics* at atomic length scales (≈ 1Å = 10^{-10}m)

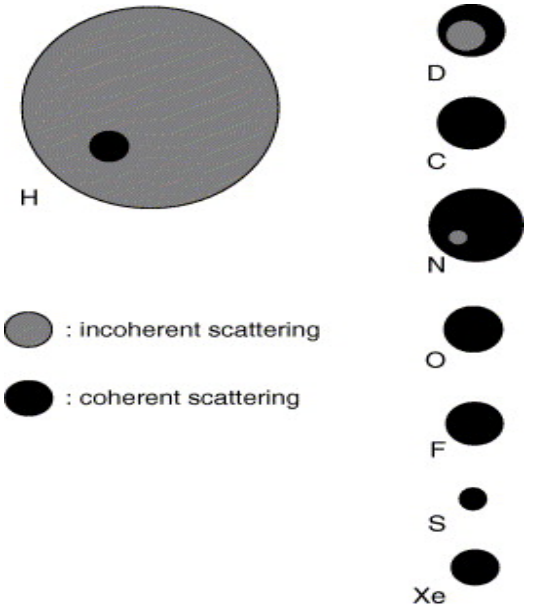
Methods – QENS



- Scatter from nucleus
- Distinguish between isotopes
- Appropriate resolution
  - ≈1Å length scale
  - ≈10 ps to ≈10 ns time scale

Methods – Why QENS?

- Contrast Matching
  - Replacing hydrogen (H) with deuterium (D) allows us to choose which particle to look at
- Coherent vs Incoherent Scattering
  - Coherent: multiple particles
  - Incoherent: single particles
  - Looking at clusters means focusing on coherent data



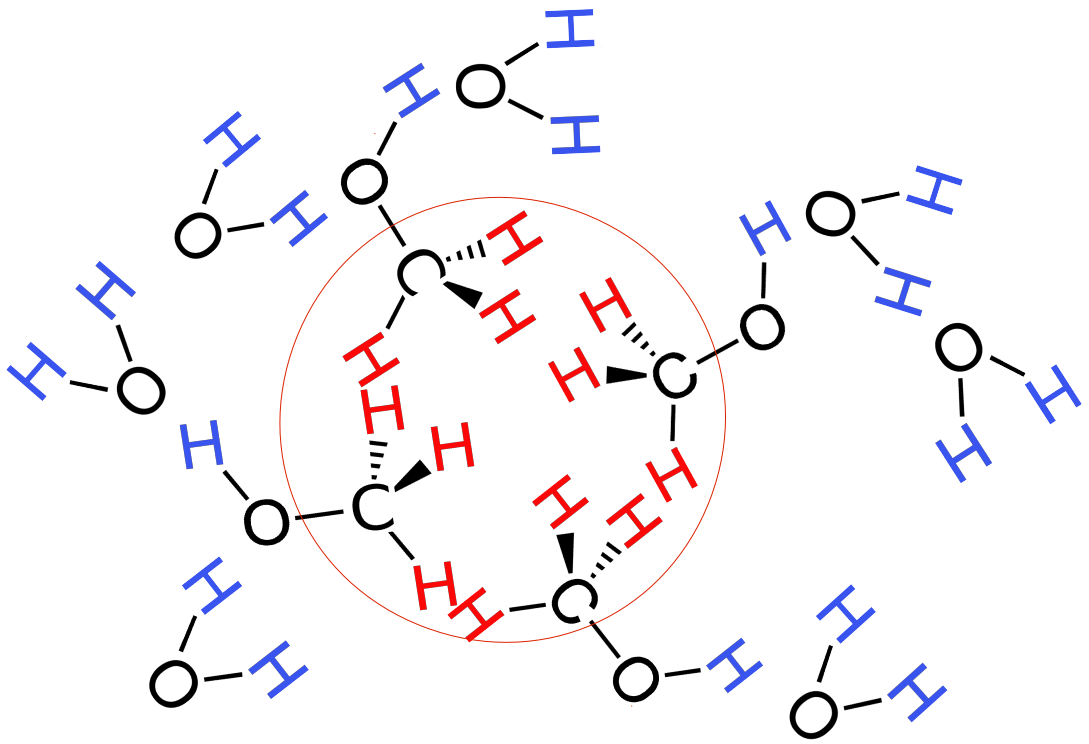
Atom	Coherent	Incoherent
Hydrogen	1.76	80.3
Deuterium	5.59	2.05
Carbon	5.56	0.0
Oxygen	4.23	0.0

Methods – Subtraction

- $CD_3OH/H_2O + CH_3OD/D_2O - (CH_3OH/H_2O + CD_3OD/D_2O)$

$- 6 (b_D - b_H)^2 S(H_M H_W)(1-x_M)x_M - 3 (b_D - b_H)^2 S(H_M H_{MH})x_M^2$

- Cancel incoherent signal
- Show distance correlations between methyl groups (H_M) and hydroxyl groups (H_{MH}, H_W)



Instruments

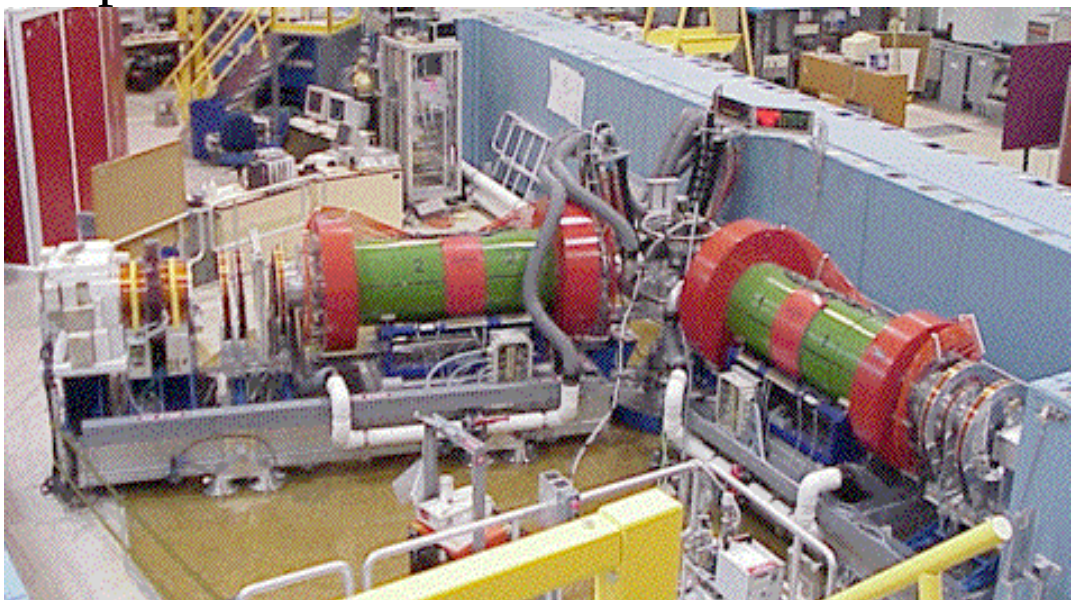
- Structure: Measure S(Q)
  - Triple-Axis Spectrometer (SPINS)
  - Small-Angle Neutron Scattering (SANS)
- Dynamics: Measure S(Q, E)
  - Neutron Spin-Echo
  - Disk Chopper Spectrometer (DCS)

DCS

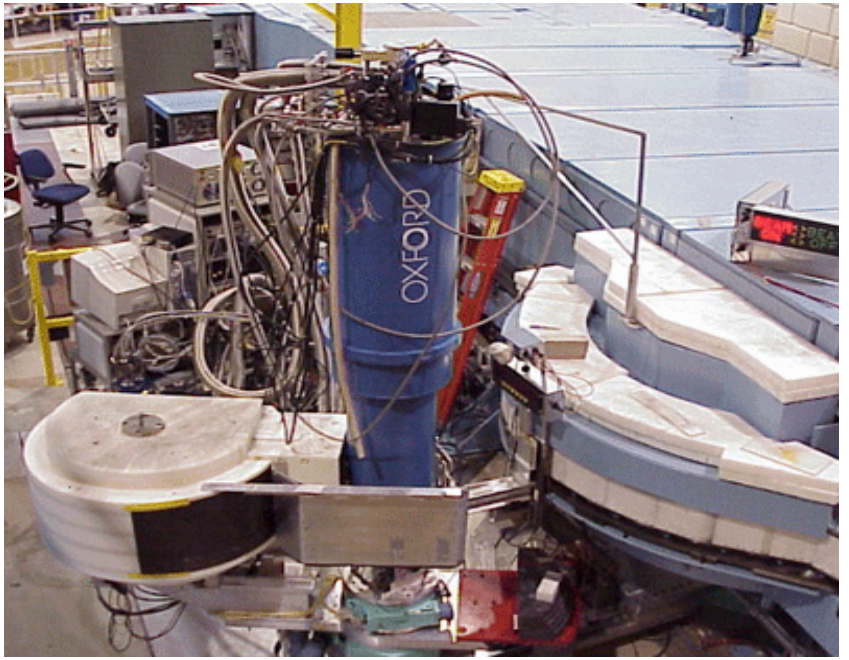
SANS

Instruments

Spin-Echo

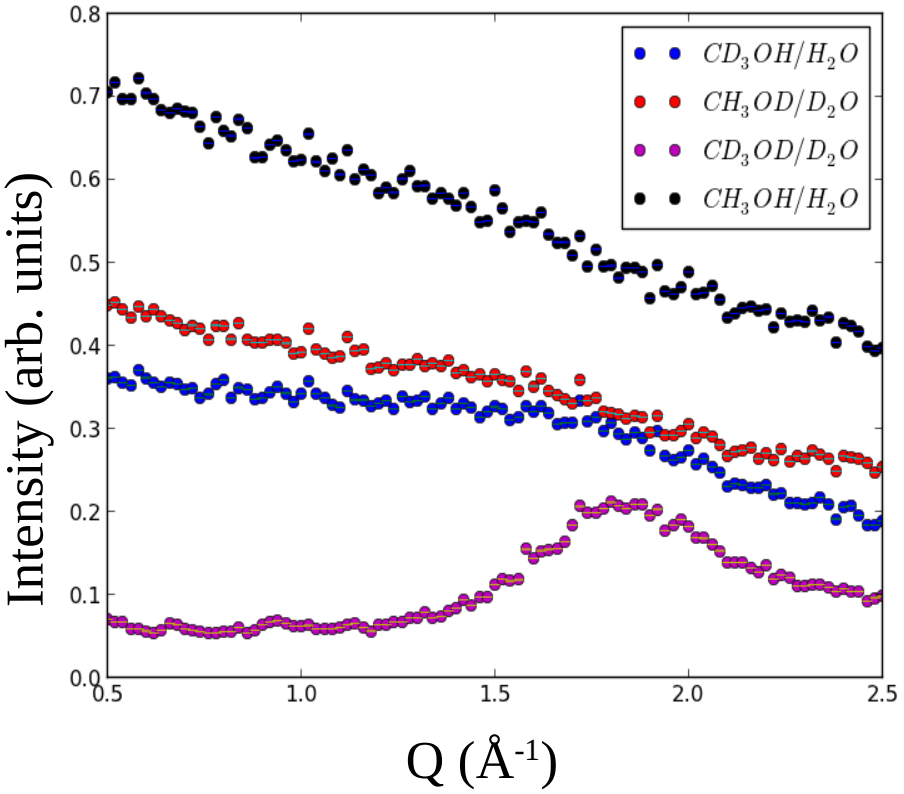


SPINS

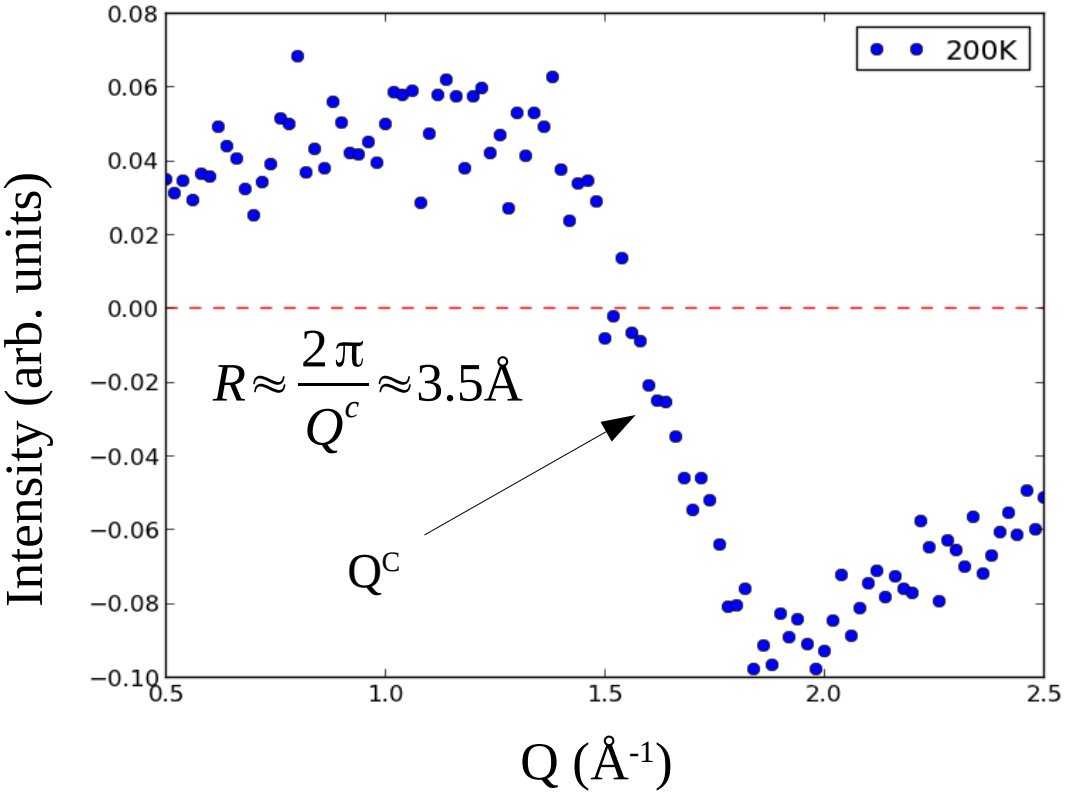


Results - Structure

SPINS Data



Subtraction

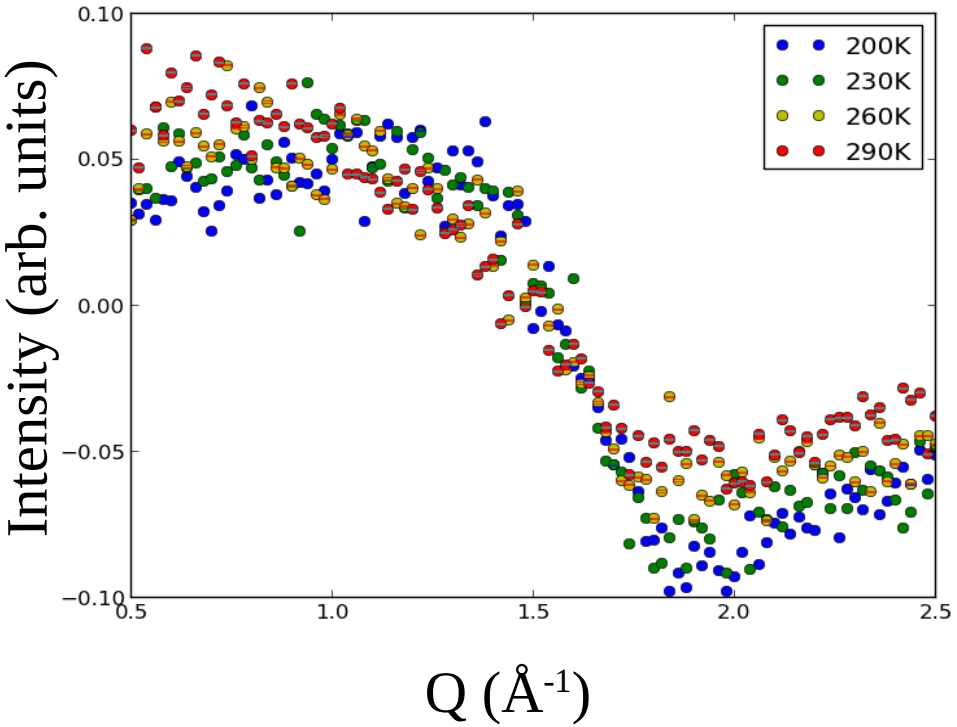


- Subtracted signal indicates structuring (not flat)
- Preliminary analysis suggests a characteristic size $R \approx 3.5$Å
- More rigorous analysis and interpretation are underway.

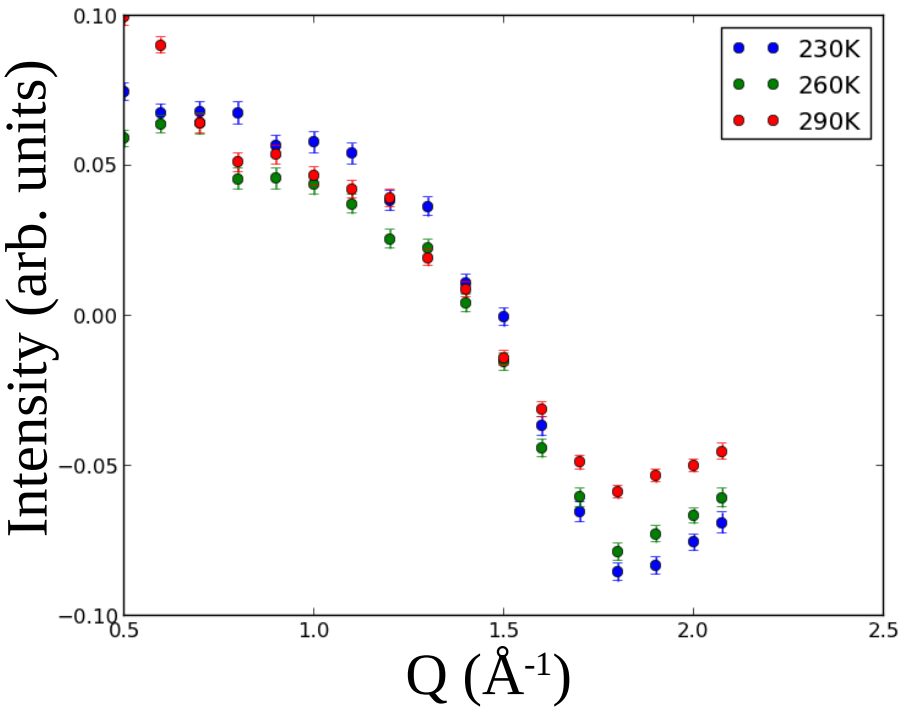
Results – Reproducibility

- Challenging experiment, small signal
  - However, results are consistent between different instruments

SPINS

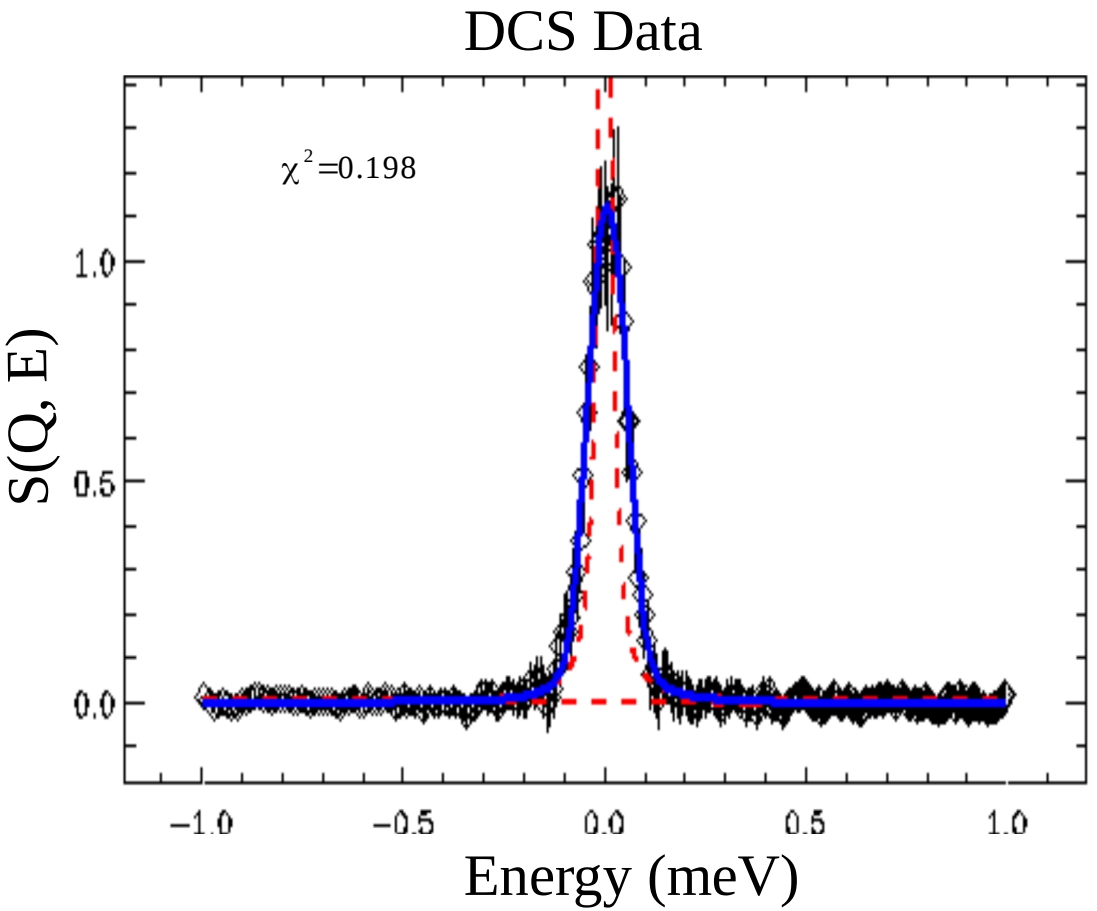


DCS



Results – Dynamics

- Subtraction can be extended to dynamics



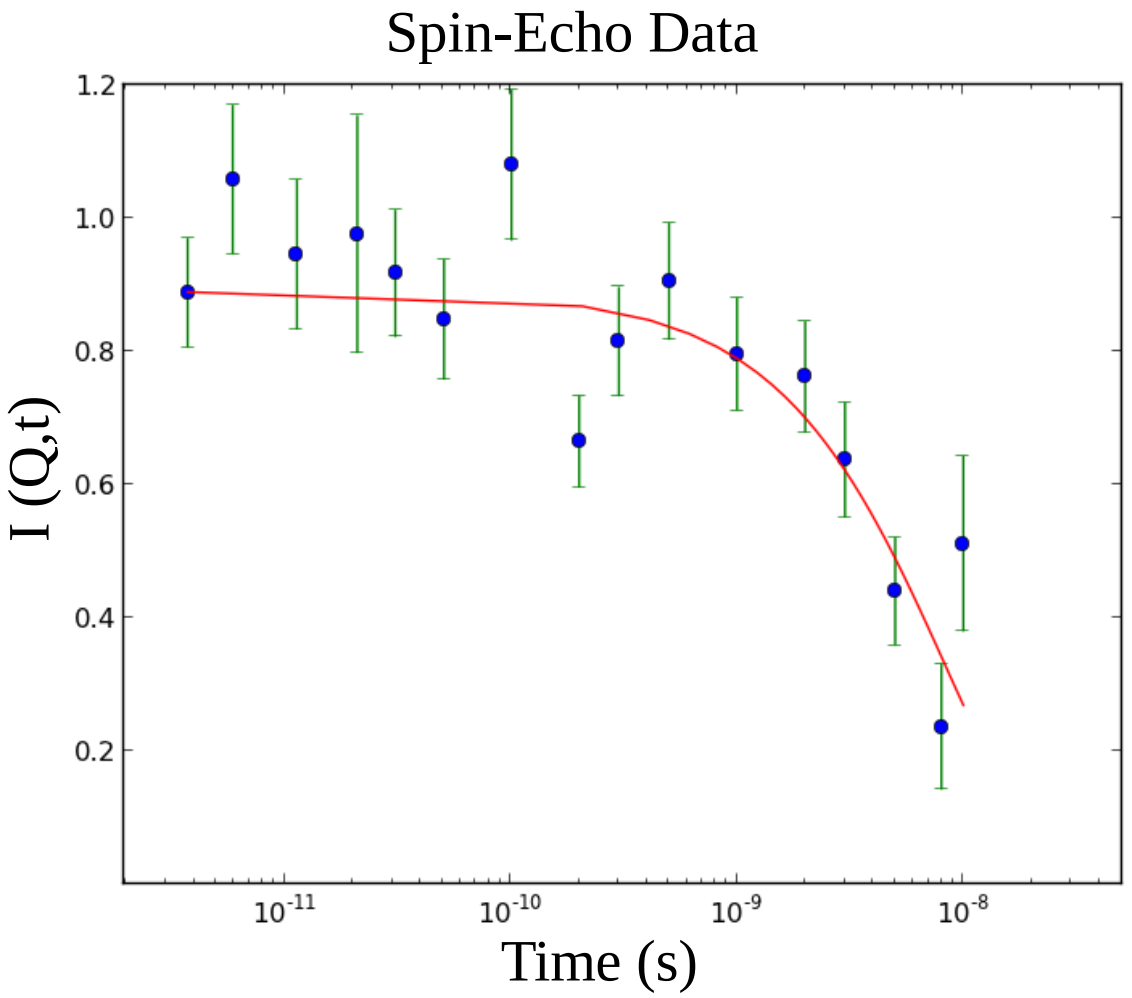
- Fit with a Lorentzian

$$S(Q,E) = A\frac{1}{\pi}\frac{\frac{\Gamma}{2}}{E^2+\left(\frac{\Gamma}{2}\right)^2} \otimes \text{Res} + \text{bkg}$$

- Width gives a timescale of motion
- Faster motion gives a broader curve

Results – Dynamics

- NSE works in the time domain measuring I(Q,t)

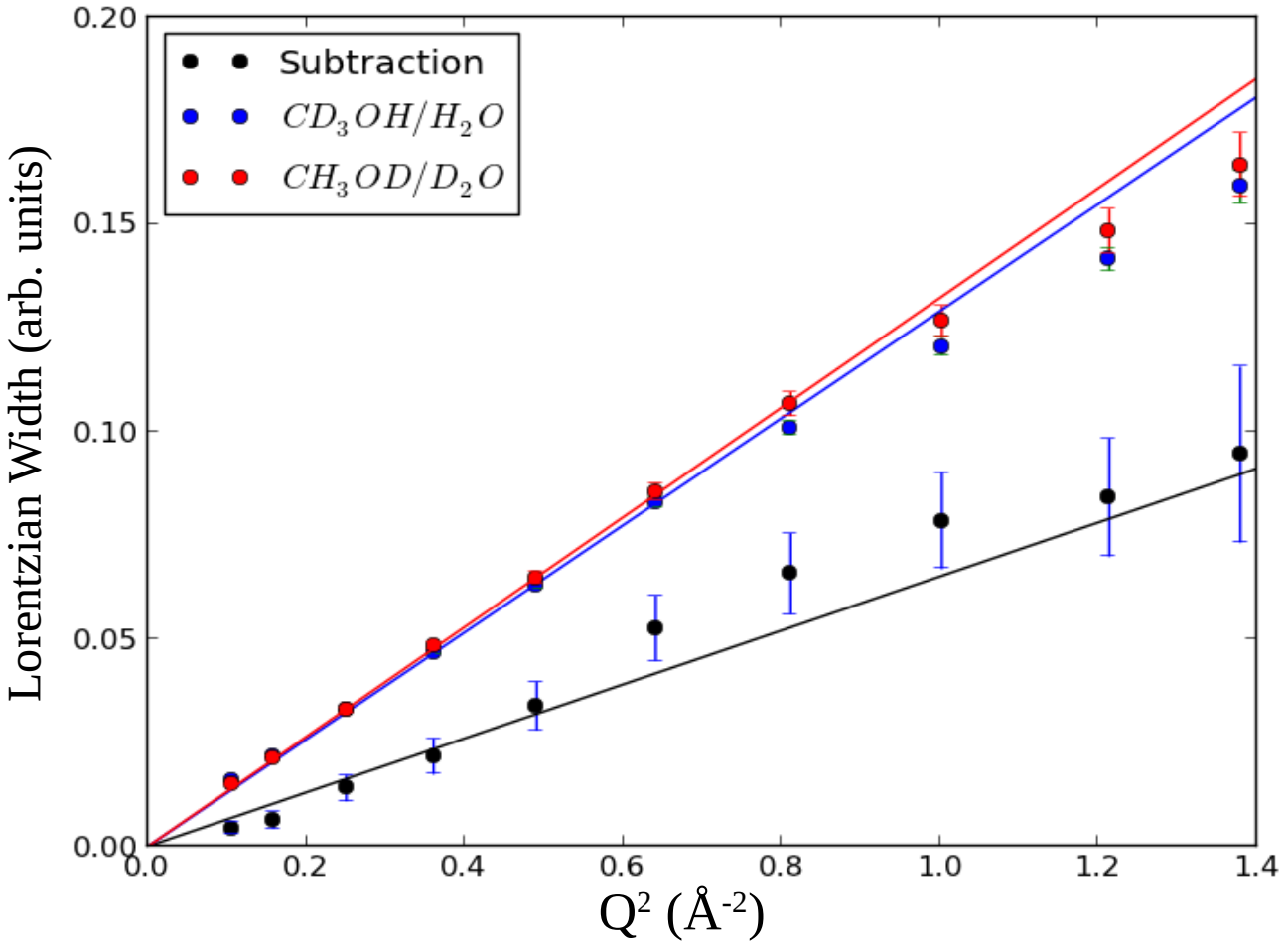


- Fit with an exponential decay

$$I(Q,t) = A\exp\left(\frac{-t}{\tau}\right)$$

- Decay rate gives a timescale of motion

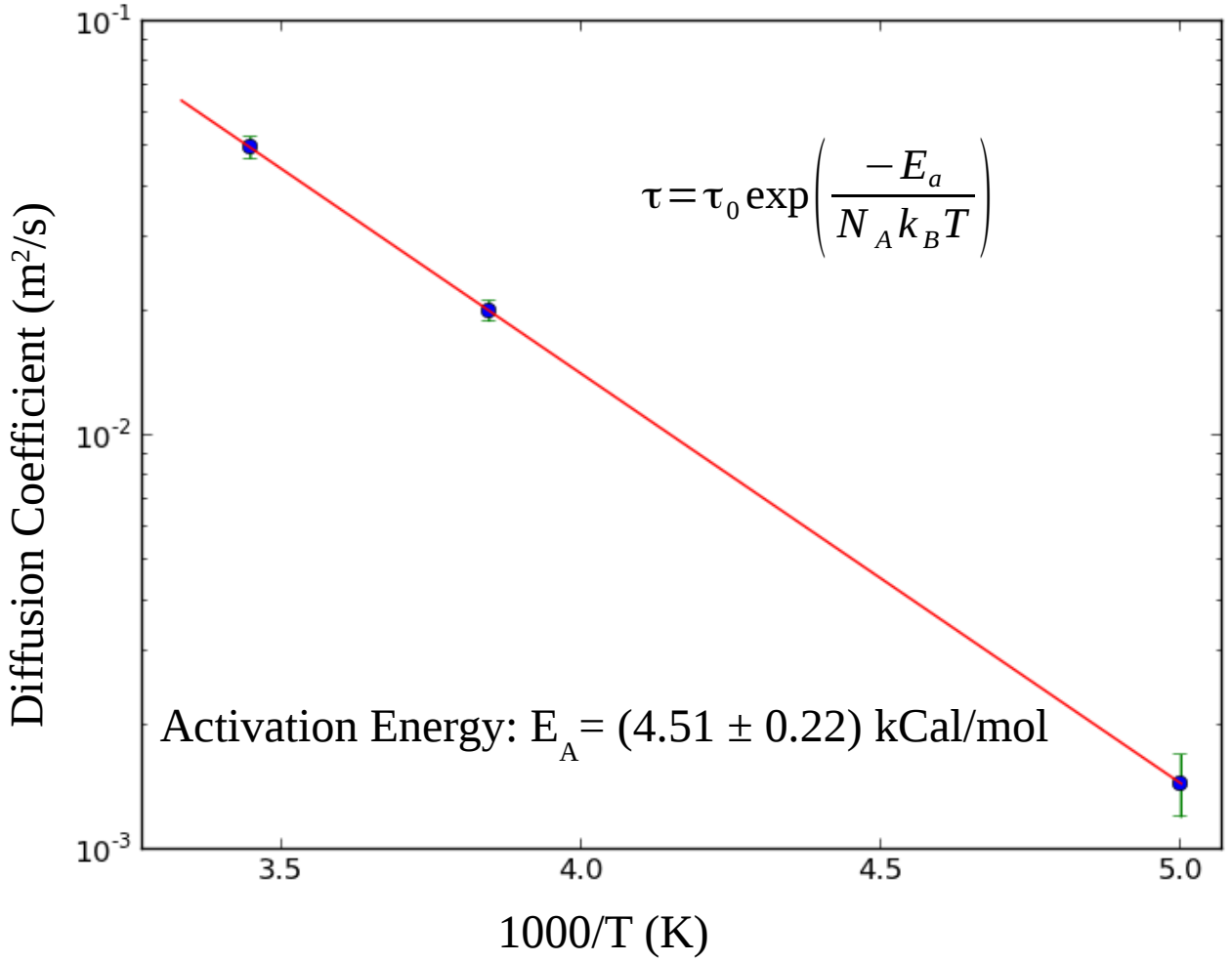
Results – Diffusive Dynamics



Dynamics measured with the subtraction method differ from the single particle dynamics

$$D = \left(6.51 \times 10^{-2} \pm 0.39 \times 10^{-2}\right) m^2/s$$

Results – Activation Energy



Conclusion

- Evidence of structuring (Clusters?)
- Successful measurement of collective (diffusive) dynamics
- Activation energy for this process
- Work in progress:
  - Interpretation
  - Comparison with single particle

Acknowledgements

- Collaborators
  - Antonio Faraone (Mentor)
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